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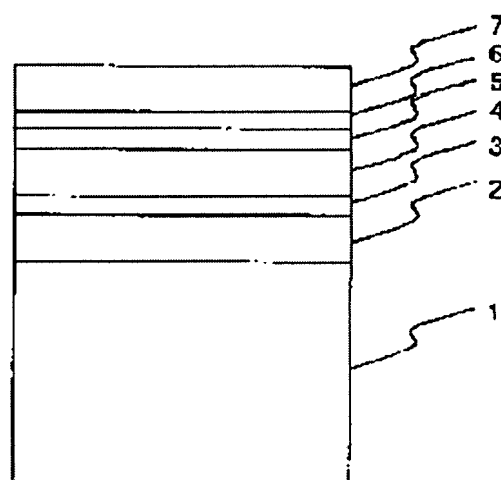(71)Applicant : SHARP CORP

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(54) FERROELECTRIC THIN FILM, SUBSTRATE COATED WITH FERRORELECTRIC THIN FILM, CAPACITOR STRUCTURE ELEMENT AND DEPOSITION OF FERROELECTRIC THIN FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To attain a high residual spontaneous polarization by shifting the compositional ratio of Bi/Ti in a ferroelectric thin film of ferroelectric crystal containing Bi, Ti and O as constitutive elements from stoichiometric composition thereby making the residual spontaneous polarization coercive electric field controllable.

SOLUTION: Surface of a silicon substrate 1, i.e., a silicon single crystal water, is thermally oxidized to form a silicon oxide layer 2. An adhesive layer 3 and a lower electrode layer 4 are then formed thereon by sputtering. Subsequently, a titanium oxide butter layer 5, a crystal nucleus layer 6, and a ferroelectric thin film 7 of ferroelectric crystal containing Bi, Ti and O as constitutive elements and having the compositional ratio of Bi/Ti shifted from stoichiometric

composition are formed further thereon. According to the structure, the residual spontaneous polarization and coercive electric field are made controllable and a high residual spontaneous polarization can be attained.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the ferroelectric thin film used for a ferroelectric memory device, a pyroelectric sensor component, a piezoelectric device, etc., a ferroelectric thin film covering substrate, a capacitor structure component, and a ferroelectric thin film.

[0002]

[Description of the Prior Art] Since a ferroelectric has many functions, such as spontaneous polarization, a high dielectric constant, the electro-optical effect, the piezo-electric effect, and a pyroelectric effect, it is applied to extensive device development, such as a capacitor, an oscillator, an optical modulator, or an infrared sensor.

[0003] Moreover, the applicable field of these ferroelectric thin films has spread with progress of thin film coating technology now. As one of them, component high integration by contraction-izing of capacitor area and improvement in dependability are achieved by applying a high dielectric constant property to the capacitor of various semiconductor devices, such as DRAM. Moreover, it is especially high-density by combination with semiconductor memory components, such as DRAM, recently, and development of the ferroelectric nonvolatile memory (FRAM) which operates at a high speed is performed briskly. Let ferroelectric nonvolatile memory be backup power supply needlessness using the strong dielectric characteristics (the hysteresis effectiveness) of a ferroelectric. A coercive electric field (Ec) is small to such device development, residual spontaneous polarization (Pr) is large, and an ingredient with properties, like the repeat resistance of polarization reversal is large is [it is low leakage current and] required for it. Furthermore, since reduction of operating voltage and a semi-conductor micro-processing process are suited, to realize the above-mentioned property with the thin film of 200nm or less of thickness is desired.

[0004] a purpose [application / to current, FRAM, etc.] -- carrying out -- thin-film-izing of lead (Pb) system oxide ferroelectrics, such as $PbTiO_3$, $Pb(Zr1-XTiX) O_3$ (PZT), and PLZT, -- the sputtering method, vacuum deposition, a sol-gel method, and MOCVD -- it is tried by the thin film formation approaches, such as law.

[0005] That in which $Pb(Zr1-XTiX) O_3$ (PZT) is studied recently most intensively, and the good thin film of strong dielectric characteristics is obtained by the sputtering method or the sol-gel method among above-mentioned ferroelectric ingredients, for example, the residual spontaneous polarization Pr has $10microC/cm2$ to $26microC/cm2$ and a big value is also obtained. However, although the strong dielectric characteristics of PZT are greatly dependent on presentation x, since they contain Pb with high vapor pressure, they have the trouble that degradation of leakage current or polarization reversal resistance takes place, with reduction (thin-film-izing) of thickness as a result of that the film presentation change in the time of membrane formation and heat treatment etc. tends to take place, generating of a pinhole, generating of the low dielectric constant layer by the reaction of the substrate electrodes Pt and Pb, etc. For this reason, development of other ingredients excellent in strong dielectric characteristics and polarization reversal resistance is desired. Moreover, when the application to an accumulation device is considered, the compactness of the thin film which can respond to micro processing is also needed.

[0006] a group which has lamellar crystal structure as shown by the following general formula as other oxide ferroelectrics -- the bismuth system oxide ferroelectric is known.

[0007] $Bi2Am-1BmO3m+3$ -- A is chosen from $Na1+$, $K1+$, $Pb2+$, calcium2+, $Sr2+$, $Ba2+$, and $Bi3+$, B is chosen from $Fe3+$, $Ti4+$, $Nb5+$, $Ta5+$, $W6+$, and $Mo6+$ here, and m is the one or more natural numbers. The base of the crystal structure of a ferroelectric expressed with this general formula constitutes the structure between which $2(Bi 2O2)+$ layers put the upper and lower sides of the stratified perovskite layer with which the perovskite grid which consists of ABO_3 of an individual (m-1) was

connected. In these ingredients, many ingredients which combined what was chosen from Sr, Ba, and Bi as A, and the thing chosen from Ti, Ta, and Nb as B show a ferroelectricity.

[0008] Also in the ferroelectric shown by the above-mentioned general formula, Bi4Ti 3O12 (titanic-acid bismuth) is a ferroelectric with the strong stratified perovskite structure (a prismatic crystal/lattice constant: a= 5.411A, c= 32.83A) of an anisotropy. And the ferroelectricity of the single crystal is compared with residual spontaneous polarization Pr=50microC/cm2 and coercive electric field Ec=50 kV/cm in the direction of an a-axis, compares it with residual spontaneous polarization Pr=4microC/cm2, coercive electric field Ec=4 kV/cm, and other above-mentioned bismuth system oxide ferroelectrics in the direction of a c-axis, is the largest, and is very small. [of the value of the direction of a c-axis of the coercive electric field] [of the value of the direction of an a-axis of the spontaneous polarization]

[0009] Therefore, if the stacking tendency of a thin film is controllable, and it becomes applicable to an electron device with various ferroelectric nonvolatile memory etc., it will become [since the description of the big spontaneous polarization and the small coercive electric field which this Bi4Ti 3O12 has is harnessed,]. however, c-axis oriented [with a spontaneous polarization component small what is reported by current] -- or it is one thing of the random orientation, and the present condition is fully being unable to use the big spontaneous polarization of the direction of an a-axis.

[0010] on the other hand -- thin-film-izing of Bi4Ti 3O12 -- until now -- MOCVD -- it is tried by law or the sol gel process. Among these, the ferroelectric thin film formation using the conventional sol gel process needed heat treatment of 650 degrees C or more, in order to obtain good strong dielectric characteristics, and since film surface morphology consisted of crystal grain which is about 0.5 micrometers further, it was difficult to apply to the high accumulation device which needs micro processing. Moreover, since 3OBi4Ti12 c-axis oriented thin film is 600 degrees C or more in substrate temperature and is carried out on Pt electrode layer / SiO2 insulator layer / Si substrate, or Pt substrate, the ferroelectric thin film formation by the MOCVD method is not applicable to actual device structure as it is. That is, like a Pt/SiO2/Si substrate, in order to secure the bond strength of Pt electrode layer and SiO2 film under it, glue lines, such as Ti film, are required between Mr. [Pt electrode layer and / SiO2 film] however, Pt electrode substrate top which prepared such a glue line -- 3OBi4Ti12 thin film -- MOCVD -- the film surface morphology, when it produces by law While consisting of big and rough crystal grain Becoming easy to generate a pyrochlore phase (Bi2Ti 2O7) is reported (Jpn.J.Appl.Phys., 32 and 1993, pp.4086 and J.Ceramic Soc.Japan, 102 and 1994, pp.512 reference). If film surface morphology consists of big and rough crystal grain, in being inapplicable to the high accumulation device which needs micro processing, and thin thickness, it will become the cause of a pinhole and will become cod roe also about generating of leakage current. Therefore, it is in a difficult situation to realize the ferroelectric thin film which has good strong dielectric characteristics by thin thickness 200nm or less with such a conventional technique.

[0011]

[Problem(s) to be Solved by the Invention] As mentioned above, with the above-mentioned conventional technique, the problem that the large spontaneous polarization property of the direction of an a-axis of Bi4Ti 3O12 is not fully harnessed, and although a ferroelectric thin film is applied to a high accumulation device again, it has technical problems -- the compactness or surface smoothness on micro processing or the front face of a thin film required for low leakage current are not obtained.

[0012] This invention is made in order to solve the above technical problems, it makes controllable residual spontaneous polarization and a coercive electric field, and it can acquire big residual spontaneous polarization, and the front face of a thin film is still precise and flatter, and it aims at offering the manufacture approach of the ferroelectric thin film excellent in the leak current characteristic, a ferroelectric thin film covering substrate, a capacitor structure component, and a ferroelectric thin film.

[0013]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, in this invention, it is considering as the ferroelectric thin film with which the presentation ratio of Bi/Ti in the

account ferroelectric thin film shifted from stoichiometric composition in the ferroelectric thin film which consists of the ferroelectric crystal which contains Bi, Ti, and O as a configuration element.

[0014] According to this invention, since the residual spontaneous polarization and the coercive electric field of a ferroelectric thin film are controllable, according to the property for which the electron device to which the ferroelectric thin film is applied is asked, it becomes possible to design a ferroelectric thin film freely.

[0015] Furthermore, in this invention, in the above-mentioned ferroelectric thin film, the ferroelectric crystal consists of a titanic-acid bismuth, and the presentation ratio of Bi/Ti in the ferroelectric thin film is carrying out to 1.5 or less [0.7 or more].

[0016] Since according to this invention the c-axis oriented component and a-axis oriented component of the stacking tendency will be controlled and the residual spontaneous polarization and the coercive electric field of a ferroelectric thin film can be controlled by this by setting up the presentation ratio of Bi/Ti of a titanic-acid bismuth ferroelectric thin film or less [0.7 or more] by 1.5, according to the property for which the electron device to which the ferroelectric thin film is applied is asked, it becomes possible to design a ferroelectric thin film freely.

[0017] Furthermore, in this invention, in the above-mentioned ferroelectric thin film, the ferroelectric crystal consists of a titanic-acid bismuth, and the presentation ratio of Bi/Ti in said ferroelectric thin film is carrying out to 1.5 or less more greatly than 1.33.

[0018] Since the a-axis oriented component of the stacking tendency is greatly utilizable by setting more greatly than 1.33 the presentation ratio of Bi/Ti of a titanic-acid bismuth ferroelectric thin film or less from 1.5, i.e., stoichiometry, to overBi according to this invention, the residual spontaneous polarization of a ferroelectric thin film can be raised sharply by this, and it becomes possible to extend the application range of an electron device greatly.

[0019] And the above-mentioned ferroelectric thin film is arranged through the buffer layer which consists of titanium oxide on a substrate, and the ferroelectric thin film covering substrate consists of this inventions.

[0020] According to this invention, since the titanium oxide buffer layer is prepared, the strong dielectric characteristics of a ferroelectric thin film can be raised, and the ferroelectric thin film which has the above outstanding properties can be realized.

[0021] Furthermore, in the above-mentioned ferroelectric thin film covering substrate, the crystalline-nucleus layer used as the growth nucleus of the ferroelectric crystal which accomplishes the ferroelectric thin film between a buffer layer and a ferroelectric thin film arranges and consists of this inventions.

[0022] According to this invention, since the crystalline-nucleus layer is prepared, the crystallinity of a ferroelectric thin film can be raised and the ferroelectric thin film which has the above outstanding properties can be realized.

[0023] And the above-mentioned ferroelectric thin film constitutes the capacitor structure component from this invention as capacitor structure inserted into the electrode of a lot at least.

[0024] Since the ferroelectric thin film which has the above outstanding properties is used according to this invention, the capacitor structure component excellent in many properties is realizable.

[0025] And a lower electrode is arranged between a substrate and a buffer layer, on the above-mentioned ferroelectric thin film, an up electrode is arranged and the capacitor structure component consists of this inventions as capacitor structure.

[0026] Since the ferroelectric thin film which has the above outstanding properties is used according to this invention, the capacitor structure component excellent in many properties is realizable.

[0027] Moreover, in the manufacture approach of the ferroelectric thin film which consists of the ferroelectric crystal which contains Bi, Ti, and O as a configuration element, the stacking tendency of the ferroelectric crystal in this ferroelectric thin film is controlled by this invention by changing the presentation ratio of Bi/Ti in a ferroelectric thin film.

[0028] According to this invention, since the stacking tendency of the ferroelectric crystal in a ferroelectric thin film is controlled, according to the property for which the electron device to which the ferroelectric thin film which can control the residual spontaneous polarization and the coercive electric

field of a ferroelectric thin film is applied is asked, it becomes possible to design a ferroelectric thin film freely.

[0029] Furthermore, in the manufacture approach of the above-mentioned ferroelectric thin film, the c-axis oriented component and orientation (117) component of a stacking tendency of a ferroelectric crystal in the ferroelectric thin film are controlled by this invention by a ferroelectric crystal's consisting of a titanic-acid bismuth, and changing the presentation ratio of Bi/Ti in the ferroelectric thin film in the or more 0.7 1.5 or less range.

[0030] In this invention, the c-axis oriented component and (117) orientation component of the stacking tendency are controlled by setting up the presentation ratio of Bi/Ti of a titanic-acid bismuth ferroelectric thin film or less [0.7 or more] by 1.5. Since this (117) orientation component contains many a-axis oriented components, according to this invention, it can control the residual spontaneous polarization and the coercive electric field of a ferroelectric thin film by control of such a stacking tendency, and becomes possible [designing a ferroelectric thin film freely] according to the property for which the electron device to which that ferroelectric thin film is applied is asked.

[0031] furthermore, the manufacture approach of the ferroelectric thin film above-mentioned in this invention -- setting -- MOCVD -- Bi material gas and Ti material gas are supplied by law, a ferroelectric thin film is formed on a substrate, and the presentation ratio of Bi/Ti in the ferroelectric thin film is changed by [of Bi material gas at the time of the ferroelectric thin film formation, or Ti material gas] controlling one of the amount of supply at least.

[0032] MOCVD which was excellent in mass-production nature according to this invention -- it becomes controllable [the stacking tendency of a titanic-acid bismuth ferroelectric thin film] using law.

[0033] Furthermore, in this invention, in the manufacture approach of the above-mentioned ferroelectric thin film, after forming the buffer layer which consists of titanium oxide on a substrate, the ferroelectric thin film is formed.

[0034] Since according to this invention the ferroelectric thin film is formed after forming a titanium oxide buffer layer, the ferroelectric thin film excellent in strong dielectric characteristics can be formed, and the ferroelectric thin film which has the above outstanding properties can be realized.

[0035] furthermore, the crystalline-nucleus layer used as the growth nucleus of the ferroelectric crystal which forms the buffer layer which consists of titanium oxide on a substrate in the manufacture approach of the above-mentioned ferroelectric thin film in this invention, and accomplishes a ferroelectric thin film on the buffer layer -- 450-degree-C or more membrane formation temperature of 650 degrees C or less -- MOCVD -- after forming by law, the ferroelectric thin film is formed on the crystalline-nucleus layer.

[0036] Since according to this invention the ferroelectric thin film is formed after forming a crystalline-nucleus layer, the ferroelectric thin film excellent in crystallinity can be formed, and the ferroelectric thin film which has the above outstanding properties can be realized.

[0037]

[Embodiment of the Invention] Hereafter, one gestalt of operation of this invention is explained with reference to a drawing. Drawing 1 is drawing showing the structure of the ferroelectric thin film covering substrate which is the 1st operation gestalt of this invention. As shown in drawing 1 , sequential formation of the ferroelectric thin film 7 with which this capacitor structure component consisted of the silicon oxide (SiO2) layer 2, a glue line 3, the lower electrode 4, the titanium oxide buffer layer 5, the crystalline-nucleus layer 6, and the ferroelectric crystal that contains Bi, Ti, and O as configuration elements on the silicon (Si) substrate 1, and the presentation ratio of Bi/Ti shifted from stoichiometric composition is carried out, respectively.

[0038] the 1st operation gestalt -- as a silicon substrate 1 -- a silicon single crystal wafer -- using -- SiO two-layer -- the silicon oxide thin film which oxidizes thermally a silicon single crystal wafer front face as 2, and is obtained was used. moreover -- as a glue line 3 -- a tantalum (Ta) thin film -- as the lower electrode 4 -- a platinum (Pt) thin film -- as a crystalline-germ layer 6, as a ferroelectric thin film 7, the titanic-acid bismuth thin film (3OBi4Ti12 thin film) was used, and the platinum (Pt) thin film was used

for the titanic-acid bismuth thin film (3OBi4Ti12 thin film) as an up electrode 6, respectively.

[0039] Next, the manufacture approach of the ferroelectric thin film covering substrate of the 1st operation gestalt shown in drawing 1 is explained. First, production of a Pt/Ta/SiO2/Si substrate is explained. oxidizing thermally the front face of the silicon single crystal wafer (100) side which is a silicon substrate 1 -- the SiO two-layer of 200nm of thickness -- 2 is formed. And it is 30nm of thickness about Ta thin film which is a glue line 3, and Pt (111) thin film which is the lower electrode layer 4 was formed by the spatter by 200nm of thickness, respectively.

[0040] In addition, such ingredients or thickness are not limited to this operation gestalt, and a polycrystal silicon substrate, a GaAs substrate, etc. may be used for them instead of a silicon single crystal substrate here. Moreover, a glue line prevents exfoliation of the film resulting from the coefficient of thermal expansion of a substrate and a lower electrode layer differing during membrane formation, and it is [that what is necessary is just extent which can prevent exfoliation of the film] desirable [thickness] in the case of this operation gestalt, since the alloy of Ti and Pt is formed, although things can be carried out to use [which uses titanium (Ti) etc. also about an ingredient in addition to Ta] Ta. moreover, the thing by which the SiO two-layer used for the insulating layer was produced by thermal oxidation -- you may not be -- a spatter, a vacuum deposition method, and MOCVD -- SiO2 film, a silicon nitride film, etc. which were formed of law etc. can be used, and an ingredient and thickness should just fully have insulation.

[0041] Moreover, although the conductive ingredient which is not limited to Pt and used for the usual electrode material is [that what is necessary is just to be] sufficient as an ingredient a grade, it is the thing on which thickness can fully function as an electrode layer also about a lower electrode and which can be suitably chosen in connection with other thin films. Moreover, the membrane formation approach is also limited to neither silicon thermal oxidation nor a spatter, and may be performed using the usual thin film coating technology, such as a vacuum deposition method. Moreover, substrate structure is not limited to the above-mentioned thing, either.

[0042] subsequently, the Bi4Ti3O12 ferroelectric thin film which is the ferroelectric thin film 7 with which it consisted of the Bi4Ti3O12 crystalline-nucleus layer which are the titanium oxide buffer layer 5 and the crystalline-nucleus layer 6, and the ferroelectric crystal which contains Bi, Ti, and O as configuration elements, and the presentation ratio of Bi/Ti shifted from stoichiometric composition on the Pt/Ta/SiO2/Si substrate which carried out in this way and was produced -- one by one -- MOCVD -- it formed by law.

[0043] First, membrane formation of a titanium oxide buffer layer set substrate temperature as 400 degrees C, carried out the heating evaporation of this raw material at 50 degrees C, using a titanium iso PUROPOKI side (Ti4 (i-OC3H7)) as a Ti raw material, supplied it with Ar carrier gas (flow rate 50sccm), and formed the titanium oxide buffer layer whose thickness is 50nm. In this membrane formation process, since gaseous phase reaction became it easy to occur to be 10 or more Torrs, the degree of vacuum of the membrane formation interior of a room was set to 5Torr. In addition, as membrane formation temperature at the time of titanium oxide buffer layer membrane formation (substrate temperature), 350-600 degrees C is desirable, and if it is the range of 1-10nm as thickness of a titanium oxide buffer layer, it can be checking achieving the function as a buffer layer here.

[0044] Membrane formation of a Bi4Ti3O12 crystalline-nucleus layer and a Bi4Ti3O12 ferroelectric thin film was succeedingly performed on the titanium oxide buffer layer after membrane formation of a titanium oxide buffer layer on the membrane formation conditions shown in Table 1.

[0045]

[Table 1]

原料	B i (o－C₇H₇)₃	T i (i－O C₃H₇)₄
原料温度	1 6 0 ℃	5 0 ℃
キャリアガス（A r）流量	1 5 0 ～ 3 0 0 sccm	5 0 sccm
反応ガス（O₂）流量	1 0 0 0 sccm	
成膜室内ガス圧力	5 T o r	
基板	P t／T a／S i O₂／S i （100）	
基板温度（成膜温度）	結晶核層:600℃，強誘電体薄膜:400℃	

[0046] Membrane formation of a Bi4Ti3O12 crystalline-nucleus layer and a Bi4Ti3O12 ferroelectric thin film As shown in Table 1, as a Bi raw material a TORIORUTO tolyl virile bismuth (Bi3 (o-OC7H7)) A titanium iso PUROPOKI side (Ti4 (i-OC3H7)) is used as a Ti raw material, respectively. Heating evaporation was carried out at the raw material temperature which shows these raw materials in Table 1, respectively (160 degrees C of Bi raw materials, 50 degrees C of Ti raw materials), and the membrane formation interior of a room was supplied with the oxygen (O2) gas which is the argon (Ar) gas and reactant gas which are carrier gas. Here, the flow rate at the time of Ar gas supply was changed by 150 - 300sccm to Bi raw material, and was set to fixed 50sccm(s) to Ti raw material, and the flow rate at the time of O2 gas supply was set to 1000sccm(s) (fixed). In addition, also in these membrane formation processes, the degree of vacuum of the membrane formation interior of a room was set to 5Torr like the time of titanium oxide buffer layer membrane formation.

[0047] On the above conditions, membrane formation temperature, i.e., substrate temperature, is first set as 600 degrees C. Thickness forms the Bi4Ti3O12 crystalline-nucleus layer which is 5nm, and sets membrane formation temperature (substrate temperature) as 400 degrees C. By forming a Bi4Ti3O12 ferroelectric thin film by the same Bi material gas flow rate (Ar carrier gas flow rate to Bi material gas) as a Bi4Ti3O12 crystalline-nucleus layer The titanium oxide buffer layer, the crystalline-nucleus layer, and the ferroelectric thin film covering substrate as shown in drawing 1 all whose thickness of a ferroelectric thin film is 100nm were produced.

[0048] In production of the above-mentioned ferroelectric thin film covering substrate, the amount of supply of Bi material gas was controlled by changing Ar carrier gas flow rate of Bi material gas in the range of 150 - 300sccm at the time of membrane formation of a Bi4Ti3O12 crystalline-nucleus layer and a Bi4Ti3O12 ferroelectric thin film. As a result of Bi material gas flow rate at that time (Ar carrier gas flow rate to Bi material gas) producing 150, 170, 180, 190, 200, 220, 230, 250, and nine kinds of things of 300sccm(s) and carrying out the component analysis of the Bi/Ti presentation ratio of the Bi4Ti3O12 ferroelectric thin film using EPMA, it came to be shown in Table 2.

[0049]
[Table 2]

B i 原料ガス流量(sccm)	150	170	180	190	200	220	230	250	300
B i／T i 組成比	0.5	0.7	0.8	0.9	1.0	1.22	1.33	1.42	1.47

[0050] Drawing in which plotting a Bi/Ti presentation ratio on an axis of abscissa, plotting each for Bi material gas flow rate (Bi flow rate) on an axis of ordinate, and showing those relation based on the result of Table 2 is drawing 2 . When a Bi/Ti presentation ratio is smaller than the stoichiometry (Bi/Ti=1.33) of Bi4Ti 3O12, the Bi/Ti presentation ratio is increasing from drawing 2 proportionally mostly with the increment in Bi material gas flow rate, but if Bi material gas flow rate becomes large

near the stoichiometry (Bi/Ti=1.33) of Bi4Ti 3O12, being in the inclination for the increment in a Bi/Ti presentation ratio to be saturated will be admitted.

[0051] Next, the above-mentioned Bi material gas flow rates differed, namely, nine kinds of ferroelectric thin film covering substrates with which Bi/Ti presentation ratios differ came to be shown in drawing 3 , as a result of investigating an X diffraction pattern. In drawing 3 , a x axis is angle-of-diffraction whenever 2theta (deg), the y-axis is X diffraction reinforcement (a. u.), and the z-axis is a Bi/Ti presentation ratio. And (n (00n) is an integer) the diffraction peak by c-axis oriented [of Bi4Ti 3O12 (stratified perovskite phase)] is expressed. (117) is a diffraction peak by the orientation containing many a-axis components (117) of Bi4Ti 3O12 (stratified perovskite phase). pyro (nnn) expresses the diffraction peak by Bi2Ti 2O7 (pyrochlore phase) of orientation (111). pyro (n00) expresses the diffraction peak by Bi2Ti 2O7 (pyrochlore phase) of orientation (100), and depends a neighboring diffraction peak (Pt (100)) on Pt of a lower electrode 2 theta= 40 degrees (deg).

[0052] Drawing 3 shows that the diffraction peak according [a Bi/Ti presentation ratio] to Bi2Ti 2O7 (pyrochlore phase) of pyro (222) or pyro (800) is observed, and Bi4Ti 3O12 (stratified perovskite phase) and Bi2Ti 2O7 (pyrochlore phase) are intermingled in 0.9 or less thing. And in 1.0 or more things, it turns out that the diffraction peak according [a Bi/Ti presentation ratio] to Bi2Ti 2O7 (pyrochlore phase) of pyro (222) or pyro (800) is not observed, but only the diffraction peak by Bi4Ti 3O12 (stratified perovskite phase) is observed, and it has a Bi4Ti3O12 single phase. In addition, although not illustrated, the Bi/Ti presentation ratio is checking being set only to Bi2Ti 2O7 (pyrochlore phase) in 0.5 or less thing.

[0053] The diffraction peak by Bi4Ti 3O12 (stratified perovskite phase) in case a Bi/Ti presentation ratio is 1.47 based on the result of the X diffraction pattern shown in drawing 3 (006), By what added (008) and the reflectivity which reaches (117) (006+008+117) The reflectivity (diffraction reinforcement) by Bi4Ti 3O12 (stratified perovskite phase) or Bi2Ti 2O7 (pyrochlore phase) is standardized. The peak intensity ratio is plotted on an axis of ordinate to the Bi/Ti presentation ratio of an axis of abscissa, and what showed the relation between an X diffraction peak intensity ratio and a Bi/Ti presentation ratio is shown in drawing 4 . In addition, it is what shows the value to which 006+008 added the reflectivity of (006) of the c-axis oriented component of Bi4Ti 3O12, and the reflectivity of (008) in drawing 4 . 117 is what shows the value of the reflectivity of (117) of the orientation (117) component of Bi4Ti 3O12. 006+007+117 shows (006) of Bi4Ti 3O12, (008), and the value that added the value of the reflectivity which reaches (117), and 222 shows the value of the reflectivity of (222) of the orientation (111) component of Bi2Ti 2O7.

[0054] the c-axis component (006) of drawing 4 to Bi4Ti 3O12 -- and (008) turns out that reflectivity is not based on change of the Bi/Ti presentation ratio in a thin film, but reflectivity (117) will increase rapidly to being almost regularity if the Bi/Ti presentation ratio in a thin film occurs or more in 0.9 and becomes more than stoichiometry (Bi/Ti=1.33).

[0055] Thus, the Bi/Ti presentation ratio in a thin film serves as c-axis oriented or less by 0.8, and an orientation component increases with the increment (117) in a Bi/Ti presentation ratio. Therefore, according to this invention, it becomes possible by changing the Bi/Ti presentation ratio in a thin film to control the c-axis oriented component and orientation (117) component of Bi4Ti 3O12 in a thin film.

[0056] In addition, in order that a Bi/Ti presentation ratio might obtain a larger ferroelectric thin film than 1.5, when still more superfluous Bi material gas flow rate was supplied at the time of a crystalline-nucleus layer and ferroelectric thin film membrane formation, the bisumuth oxide occurred in the thin film. That is, it was checked in the thin film with which the Bi/Ti presentation ratio exceeded 1.5 that the bisumuth oxide occurs. As for a Bi/Ti presentation ratio, in the ferroelectric thin film covering substrate which consists of this to a titanic-acid bismuth thin film, 1.5 or less are desirable.

[0057] In addition, since it achieves the function to become the growth nucleus of a ferroelectric thin film and to make the crystallinity inherit, what has the same crystal structure (stratified perovskite structure) as the ferroelectric thin film formed on it as the ingredient is desirable, and if a crystalline-nucleus layer is this ingredient, it is more desirable. Moreover, the thickness is having it checked that the function can be achieved by 5nm or more thickness 10nm or less. and a crystalline-nucleus layer --

MOCVD -- when forming membranes by law, as the membrane formation temperature, it is desirable to form in a 450 to 650 degrees C temperature region. In order for a crystalline-nucleus layer to be able to change with the growth nucleus of a ferroelectric thin film, 450 degrees C or more are desirable, and since a crystalline-nucleus layer can form membranes very much in a short time compared with a ferroelectric thin film, if this is 650 degrees C or less, also when applying to a high integration device, it is because it seldom becomes a problem.

[0058] Subsequently, as 2nd operation gestalt, as the structure is shown in drawing 5 , the up electrode 8 is formed on the ferroelectric thin film 7 of the ferroelectric thin film covering substrate of the 1st operation gestalt, and the result of having evaluated the electrical property about the capacitor structure component made into the capacitor structure where the ferroelectric thin film 7 was pinched between the lower electrode 4 and the up electrode 8 is explained.

[0059] In the 2nd operation gestalt, the Bi/Ti presentation ratio of a Bi4Ti3O12 ferroelectric thin film of the process to formation of the ferroelectric thin film 7 of the 1st operation gestalt is completely the same as that of the ferroelectric thin film covering substrate of 1.0 about production of a capacitor structure component. That is, Bi material gas flow rate at the time of Bi4Ti3O12 ferroelectric thin film membrane formation (Ar carrier gas flow rate to Bi material gas) is set to 200sccm. And the platinum (Pt) thin film of 100micrometerphi and 100nm of thickness was formed by the spatter as an up electrode 8 on the Bi4Ti3O12 ferroelectric thin film, and it considered as capacitor structure.

[0060] In addition, although the conductive ingredient which is not limited to Pt and used for the usual electrode material is [that what is necessary is just to be] sufficient as an ingredient a grade, it is the thing on which thickness can fully function as an electrode layer about the up electrode 8 and which can be suitably chosen in connection with other thin films. Moreover, the membrane formation approach is not limited to a spatter, either and may be performed using the usual thin film coating technology, such as a vacuum deposition method.

[0061] As a result of performing measurement of strong dielectric characteristics about the capacitor structure component of the 2nd operation gestalt, the clear hysteresis curve as shown in drawing 6 was obtained. That is, when the applied voltage between the lower electrode 4-up electrodes 8 was 3V and the applied voltage between residual spontaneous polarization Pr=5.6microC/cm2, coercive electric field Ec=59 kV/cm, and the lower electrode 4-up electrode 8 was 5V, the hysteresis curve of a configuration with good all that are called residual spontaneous polarization Pr=8.8microC/cm2 and coercive electric field Ec=66 kV/cm was obtained. In this hysteresis curve, that the bigger value than residual spontaneous polarization Pr=4microC/cm2 of the direction of a c-axis of single crystal Bi4Ti 3O12 is acquired here although the thin film of 1.0 has [this Bi/Ti presentation ratio] a strong c-axis component as compared with other things as mentioned above using drawing 3 -- reflection (117) -- **** -- it gets down and it is thought that the a-axis oriented component that to orientation (117) contained has influenced greatly. [many]

[0062] Next, the capacitor structure component of the 2nd operation gestalt came to be shown in drawing 7 , as a result of measuring a leak current characteristic (applied-voltage dependency of leak current density). It turns out that the good leak current characteristic with the small thing of the 2nd operation gestalt is shown, for example, when the applied voltage between the lower electrode 4-up electrodes 8 is 3V and the applied voltage between 4x10-8 A/cm2 and the lower electrode 4-up electrode 8 is 5V, the value of good leak current density called 1x10-7 A/cm2 is acquired from drawing 7 .

[0063] Subsequently, the result as which the Bi/Ti presentation ratio of the Bi4Ti3O12 ferroelectric thin film which is the ferroelectric thin film 7 estimated the electrical property by the structure same as 3rd operation gestalt as the capacitor structure component of the 2nd operation gestalt shown in drawing 5 about the thing of 1.47 is explained.

[0064] About production of the capacitor structure component of the 3rd operation gestalt, the Bi/Ti presentation ratio of a Bi4Ti3O12 ferroelectric thin film of the process to formation of the ferroelectric thin film 7 of the 1st operation gestalt is completely the same as that of the ferroelectric thin film covering substrate of 1.47. That is, Bi material gas flow rate at the time of Bi4Ti3O12 ferroelectric thin film membrane formation (Ar carrier gas flow rate to Bi material gas) is set to 300sccm. And on the

Bi4Ti3O12 ferroelectric thin film, like the 2nd operation gestalt, the platinum (Pt) thin film was formed by the spatter as an up electrode 8, and it considered as capacitor structure.

[0065] As a result of performing measurement of strong dielectric characteristics about the capacitor structure component of the 3rd operation gestalt, the clear hysteresis curve as shown in drawing 8 was obtained. When the applied voltage between the lower electrode 4-up electrodes 8 is 3V, namely, residual spontaneous polarization Pr=12.0microC/cm2, coercive electric field Ec=104 kV/cm, When the applied voltage between the lower electrode 4-up electrodes 8 is 5V, residual spontaneous polarization Pr=23.6microC/cm2, coercive electric field Ec=136 kV/cm, When the applied voltage between the lower electrode 4-up electrodes 8 was 6V, the hysteresis curve in which all that are called residual spontaneous polarization Pr=25.0microC/cm2 and coercive electric field Ec=138 kV/cm have very big residual spontaneous polarization in a good configuration was obtained. It is because it is strongly influenced for the a-axis oriented component which the thin film of 1.47 has [this Bi/Ti presentation ratio / as mentioned above using ** from which the value of big such residual spontaneous polarization was acquired in this hysteresis curve here, and drawing 3 / other things] the largest reflection (117), serves as a thin film with the strongest stacking tendency (117), and is contained.

[0066] Next, the capacitor structure component of the 3rd operation gestalt came to be shown in drawing 9 , as a result of measuring a leak current characteristic (applied-voltage dependency of leak current density). Drawing 9 shows that the good leak current characteristic with the small thing of the 3rd operation gestalt is shown. For example, when the applied voltage between the lower electrode 4-up electrodes 8 is 3V and the applied voltage between 8x10-9 A/cm2 and the lower electrode 4-up electrode 8 is 5V, the value of good leak current density smaller about single [more] figure than the thing of the 2nd operation gestalt of 2x10-8 A/cm2 is acquired. In a leak current characteristic, it is possible that the crystallinity of a thin film is excellent in the direction of the thing of the 3rd operation gestalt as one cause whose thing of the 3rd operation gestalt improved rather than the thing of the 2nd operation gestalt.

[0067] Thus, according to the 3rd operation gestalt, very big residual spontaneous polarization was acquired. This shows that the a-axis oriented component of Bi4Ti 3O12 is greatly utilizable, and shows that very big residual spontaneous polarization is acquired in a ferroelectric thin film with a strong orientation (117) component. Therefore, as the 1st operation gestalt also explained, when big residual spontaneous polarization is acquired in that to which an orientation (117) component becomes strong and the presentation ratio of Bi/Ti in a Bi4Ti3O12 ferroelectric thin film becomes it is large and more superfluous [Bi] than 1.5 or less, i.e., stoichiometry, from 1.33, big residual spontaneous polarization is acquired.

[0068] From the evaluation result of the electrical property of the 2nd of a more than, and the 3rd operation gestalt, even if all the thickness of a titanium oxide buffer layer, a Bi4Ti3O12 crystalline-nucleus layer, and a Bi4Ti3O12 ferroelectric thin film is the very thin thickness of 100nm Since the small good leak current characteristic was shown and outstanding strong dielectric characteristics were shown, the result investigated about the surface morphology of these ferroelectric thin films is explained as 4th operation gestalt.

[0069] In the ferroelectric thin film covering substrate of what does not form the up electrode 8 in the 2nd operation gestalt with the 4th operation gestalt, i.e., the 1st operation gestalt Bi material gas flow rate at the time of Bi4Ti3O12 ferroelectric thin film membrane formation (Ar carrier gas flow rate to Bi material gas) is set to 200sccm(s). The Bi/Ti presentation ratio of a Bi4Ti3O12 ferroelectric thin film 1.0 things, In the ferroelectric thin film covering substrate of what does not form the up electrode 8 in the 3rd operation gestalt, i.e., the 1st operation gestalt Bi material gas flow rate at the time of Bi4Ti3O12 ferroelectric thin film membrane formation (Ar carrier gas flow rate to Bi material gas) is set to 300sccm (s). The Bi/Ti presentation ratio of a Bi4Ti3O12 ferroelectric thin film observed those film surface morphology about two kinds of things of 1.47.

[0070] The ferroelectric thin film covering substrate and Bi/Ti presentation ratio of 1.0 show [a Bi/Ti presentation ratio] the result of having performed [which can observe the front face of a ferroelectric thin film, and the cross section of a ferroelectric thin film covering substrate] surface morphology

observation from across to drawing 10 (Bi/Ti=1.0) and drawing 11 (Bi/Ti=1.47), by SEM about the ferroelectric thin film covering substrate of 1.47, respectively. In addition, although the scale is not indicated by drawing 11 , it is the thing of the same dilation ratio as the scale indicated by drawing 10 . Drawing 10 and drawing 11 show that any ferroelectric thin film gets the minute particle of 10nm order blocked precisely, and particle size has become what has a very flat front face. Since the thin film which was excellent in this operation gestalt in this way can be formed, this serves as a cause and all the thickness of a titanium oxide buffer layer, a crystalline-nucleus layer, and a ferroelectric thin film is considered that the strong dielectric characteristics which were very excellent were shown while the small leak current characteristic of 100nm which a pinhole did not generate the thin film of these 2nd and 3rd operation gestalten, but was excellent even if very thin was shown.

[0071] Furthermore, if it excels in compactness and smooth nature in this way and a thin thin film is applied to a device, it will be very suitable for thin-film-izing and micro processing, and the application range of various high accumulation devices will be extended sharply.

[0072] here -- the Pt/Ta/SiO2/Si substrate top same as an example of a comparison as the 1st operation gestalt -- MOCVD -- at the membrane formation temperature (substrate temperature) of 600 degrees C by law Bi material gas flow rate (Ar carrier gas flow rate to Bi material gas) 230sccm(s), Ti material gas flow rate (Ar carrier gas flow rate to Bi material gas) is set to 50sccm(s), and other membrane formation conditions are explained like the 1st operation gestalt about the thing in which 3OBi4Ti12 thin film of 100nm of thickness was formed.

[0073] The result of having performed surface morphology observation from across by SEM about 3OBi4Ti12 thin film of the example of a comparison is shown in drawing 12 like the operation gestalt of the above 4th, and the result of 3OBi4Ti12 thin film mostly observed from the perpendicular direction is shown in drawing 13 , respectively. According to these, it turns out that 3OBi4Ti12 thin film of the example of a comparison consists of the huge plate crystal whose particle size is 200-500nm, and serves as surface morphology with very intense irregularity. In about 100nm thin thickness, a pinhole occurs that it is a thin film like this example of a comparison, and it is expected that a leak current characteristic deteriorates very much.

[0074] Here, if the surface morphology of the operation gestalt of the above 4th is compared with the surface morphology of the example of a comparison, it is clear how the thin film of the 4th operation gestalt by this invention is excellent in compactness and smooth nature.

[0075] Next, the result of having investigated the X diffraction pattern is shown in drawing 13 about 3OBi4Ti12 thin film of the example of a comparison. although reflection (117) of Bi4Ti 3O12 (stratified perovskite phase) can also be seen from drawing 13 -- the c-axis oriented component of Bi4Ti 3O12 (stratified perovskite phase) -- being shown (006) -- etc. (008) etc. -- a strong reflective peak -- **** -- it gets down and it turns out that c-axis oriented is a strong thin film. Moreover, it turns out that it has Bi2Ti 2O7 (222) and (444) the comparatively big reflective peak which are the orientation (111) component of Bi2Ti 2O7 (pyrochlore phase), and quite many pyrochlore phases contain.

[0076] Next, on the Bi4Ti3O12 thin film of the example of a comparison, like the above 2nd and the 3rd operation gestalt, an up electrode is formed and the result of having measured the electrical property is explained.

[0077] A hysteresis characteristic was not able to be checked when it was going to measure the strong dielectric characteristics by 3OBi4Ti12 thin film of the example of a comparison. Furthermore, when the leak current characteristic was measured, as compared with 10-3 - 10-4 A/cm2, and the above 2nd and the 3rd operation gestalt, about 4-5 figures of leak current density became [leak current density] large to the applied voltage of 3-5V. It is clear that this result's what is in agreement also with the observation result of surface morphology, and is depended on this invention is excellent in an electrical property. Moreover, by the thing of the example of a comparison, in order to show strong dielectric characteristics, even if that by which it is thought that there is need still more thickly and this depends the thickness of 3OBi4Ti12 thin film on this invention is the very thin thickness of 100nm, it is shown that outstanding strong dielectric characteristics are realizable.

[0078] In addition, if the above-mentioned operation gestalt and the example of a comparison are

contrasted, it will be thought that the ferroelectric thin film which was excellent in compactness and smooth nature, and was excellent in crystallinity was realizable with existence of a titanium oxide buffer layer and a crystalline-nucleus layer since the ferroelectric thin film was formed at the very low membrane formation temperature of 400 degrees C.

[0079] Subsequently, as 5th operation gestalt, like the 1st operation gestalt, the up electrode 8 (refer to drawing 5) is formed like the 2nd and 3rd operation gestalten on each ferroelectric thin film 7 (refer to drawing 1) of two or more ferroelectric thin film covering substrates with which the Bi/Ti presentation ratios of a ferroelectric thin film differ, it considers as a capacitor structure component, and the result of having measured those electrical properties is explained.

[0080] First, production of a ferroelectric thin film covering substrate is explained. Although the conditions of Bi material gas flow rate (Ar carrier gas flow rate to Bi material gas) were changed in membrane formation of a Bi4Ti3O12 crystalline-nucleus layer and a Bi4Ti3O12 ferroelectric thin film as shown in the above-mentioned table 2, and nine kinds of ferroelectric thin film covering substrates were produced with the 1st operation gestalt With this operation gestalt, as shown in Table 3, Bi material gas flow rate was changed, and the Bi/Ti presentation ratio of a Bi4Ti3O12 ferroelectric thin film produced 0.7, 0.8, and nine kinds of ferroelectric thin film covering substrates of 1.0, 1.1, 1.22, 1.33, 1.42, and 1.47.

[0081]
[Table 3]

B i 原料ガス流量(sccm)	170	180	190	200	210	220	230	250	300
B i ／T i 組成比	0.7	0.8	0.9	1.0	1.1	1.22	1.33	1.42	1.47

[0082] In addition, in production of the ferroelectric thin film covering substrate of this operation gestalt, it produces [all of except for the conditions of Bi material gas flow rate] like the operation gestalt of the above 1st.

[0083] Furthermore, on the Bi4Ti3O12 ferroelectric thin film of nine kinds of this ferroelectric thin film covering substrate, like the above 2nd and the 3rd operation gestalt, the up electrode 8 (refer to drawing 5) was formed, and nine kinds of capacitor structure components were produced.

[0084] Next, the result of having measured the electrical property about the capacitor structure component of this operation gestalt produced as mentioned above is explained. The result of having measured the dependency by the Bi/Ti presentation ratio (Bi/Ti) of a Bi4Ti3O12 ferroelectric thin film about the value of the residual spontaneous polarization Pr at the time of 5V impression is shown in drawing 15 . In addition, as for drawing 15 , the data of the 2nd and 3rd operation gestalten are contained. It is increasing in the field of 1.0 - stoichiometry (Bi/Ti=1.33) again gently [the Bi/Ti presentation ratio after increasing gently / the value of the residual spontaneous polarization Pr / a Bi/Ti presentation ratio / in the field of 0.7-1.0 if the Bi/Ti presentation ratio from drawing 15 increases, and increasing once rapidly / a Bi/Ti presentation ratio / in the field of 1.0-1.1]. And if a Bi/Ti presentation ratio becomes the field of stoichiometry -1.47, the value of the residual spontaneous polarization Pr is rapid with the increment in a Bi/Ti presentation ratio. In order to obtain the ferroelectric thin film which needs the value of big residual spontaneous polarization from this, it turns out that what is necessary is just to make the Bi/Ti presentation ratio larger than 1.33.

[0085] When the observation result (refer to drawing 3) of the X diffraction pattern in the operation gestalt of the above 1st is taken into consideration, the dependency over the Bi/Ti presentation ratio of such residual spontaneous polarization is the field of the Bi/Ti presentation ratio which can greatly utilize clearly, the orientation (117) component, i.e., the a-axis component, of Bi4Ti 3O12, and shows that big residual spontaneous polarization is acquired.

[0086] Next, the result of having measured the dependency by the Bi/Ti presentation ratio (Bi/Ti) of a Bi4Ti3O12 ferroelectric thin film about each value of the coercive electric field Ec at the time of 5V impression is shown in drawing 16 . In addition, as for drawing 16 , the data of the 2nd and 3rd operation gestalten are contained. If a Bi/Ti presentation ratio increases, in the value of a coercive

electric field Ec, a Bi/Ti presentation ratio is decreasing in the field of 0.7-1.0, and the Bi/Ti presentation ratio has begun to increase from drawing 16 by 1.0-1.47. In order to obtain the ferroelectric thin film which needs the value of small residual spontaneous polarization from this, it turns out that what is necessary is just to set the Bi/Ti presentation ratio about to 1.0.

[0087] in addition, the above-mentioned operation gestalt -- setting -- MOCVD -- although membrane formation temperature at the time of the Bi4Ti3O12 ferroelectric thin film membrane formation by law (substrate temperature) was made into 400 degrees C, it is not limited to this. However, when the case where it applies to a high accumulation device is assumed, in order to maintain the crystallinity of a thin film good further, 350 degrees C or more are desirable [600 degrees C or less are desirable, and]. It is such very low membrane formation temperature, and that a ferroelectric thin film can be formed enables implementation to the application to a high accumulation device.

[0088] In addition, in the above-mentioned operation gestalt, although the thing using 3OBi<SUB>4Ti12 thin film as a ferroelectric thin film was explained, this invention is not limited to this and it has a stratified perovskite structure similarly, and if it is the ferroelectric thin film which consists of the bismuth system oxide ferroelectric crystal which contains Bi, Ti, and O as a configuration element, it will be thought that it is effective.

[0089] in addition, ** limited to this although considered as the capacitor structure component which used the Pt/Ta/SiO2/Si substrate as a substrate with the above-mentioned operation gestalt -- it is -- yes. For example, you may make it a configuration which an integrated circuit is formed in Si or a GaAs substrate, and interlayer insulation films, such as silicon oxide and silicon nitride, are covered by the front face of that integrated circuit, and the electrode layer electrically connected with the element of an integrated circuit is formed on an interlayer insulation film through the contact hole formed in a part of this interlayer insulation film, and forms the ferroelectric thin film of this invention on that electrode layer. That is, this invention can apply the capacitor structure and transistor structure of the above-mentioned operation gestalt to various high accumulation devices, such as the integrated circuit device and the other ferroelectric memory devices which connected with the element of the integrated circuit made into the start electrically, a pyroelectric sensor component, and a piezoelectric device.

[0090]

[Effect of the Invention] As mentioned above, since the ferroelectric thin film which showed the strong dielectric characteristics which were very excellent also in thickness 200 micrometers or less, and was excellent in smooth nature and compactness is realizable according to this invention, it is effective in being able to raise a leak current characteristic sharply, being able to respond to various micro-processing processes, and applying to a high accumulation device.

[0091] Furthermore, according to the ferroelectric thin film of this invention, a ferroelectric thin film is controllable in the property (residual spontaneous polarization and coercive electric field) suitable for each application device by shifting the presentation ratio of Bi/Ti in a ferroelectric thin film from stoichiometry. Moreover, in the titanic-acid bismuth ferroelectric thin film, it supposes that Bi is more superfluous than the stoichiometry, namely, the very big residual spontaneous polarization of 26.23.6microC/cm2 (applied-voltage 5V) was acquired also by the thing of very thin thickness called 100nm thickness by making a Bi/Ti presentation ratio or less into 1.5 more greatly than 1.33.

[0092] Moreover, according to the manufacture approach of the ferroelectric thin film of this invention, it becomes possible by shifting the presentation ratio of Bi/Ti in a ferroelectric thin film from stoichiometry, and controlling the stacking tendency of the ferroelectric thin film to control a ferroelectric thin film in the property suitable for each application device. furthermore, not spreading membrane formation but MOCVD(s), such as the conventional MOD method and a sol-gel method, -- law is used -- since it comes out, and a thickness controllability is good, the thin film of a large area can be manufactured at a high speed and the amount of supply of the material gas at about [that productivity can be raised remarkably] and that time is only controlled, property control of a ferroelectric thin film is attained very easily. Furthermore, since a ferroelectric thin film can be formed in a low-temperature process, the ferroelectric thin film which showed the strong dielectric characteristics which were very excellent, and was excellent in smooth nature and compactness can be realized, and the thing of

applying to a high accumulation device becomes possible.

CLAIMS

[Claim(s)]
[Claim 1] The ferroelectric thin film characterized by the presentation ratio of Bi/Ti in said ferroelectric thin film having shifted from stoichiometric composition in the ferroelectric thin film which consists of the ferroelectric crystal which contains Bi, Ti, and O as a configuration element.
[Claim 2] The ferroelectric thin film with which said ferroelectric crystal consists of a titanic-acid bismuth, and the presentation ratio of Bi/Ti in said ferroelectric thin film is characterized by or more 0.7 being 1.5 or less in a ferroelectric thin film according to claim 1.
[Claim 3] The ferroelectric thin film with which said ferroelectric crystal consists of a titanic-acid bismuth, and the presentation ratio of Bi/Ti in said ferroelectric thin film is characterized by being 1.5 or less more greatly than 1.33 in a ferroelectric thin film according to claim 2.
[Claim 4] The ferroelectric thin film covering substrate which is a ferroelectric thin film covering substrate equipped with the ferroelectric thin film according to claim 1, 2, or 3, and is characterized by having been arranged through the buffer layer to which said ferroelectric thin film consists of titanium oxide on a substrate.
[Claim 5] The ferroelectric thin film covering substrate characterized by having arranged the crystalline-nucleus layer which serves as a growth nucleus of the ferroelectric crystal which accomplishes this ferroelectric thin film between said buffer layers and said ferroelectric thin films in a ferroelectric thin film covering substrate according to claim 4.
[Claim 6] The capacitor structure component characterized by being the capacitor structure component equipped with the ferroelectric thin film according to claim 1, 2, or 3, and being the capacitor structure where said ferroelectric thin film was pinched by the electrode of a lot at least.
[Claim 7] The capacitor structure component characterized by being the capacitor structure component equipped with the ferroelectric thin film covering substrate according to claim 4 or 5, and being the capacitor structure where the lower electrode has been arranged between said substrates and said buffer layers, and the up electrode has been arranged on said ferroelectric thin film.
[Claim 8] The manufacture approach of the ferroelectric thin film characterized by controlling the stacking tendency of the ferroelectric crystal in this ferroelectric thin film by changing the presentation ratio of Bi/Ti in said ferroelectric thin film in the manufacture approach of the ferroelectric thin film which consists of the ferroelectric crystal which contains Bi, Ti, and O as a configuration element.
[Claim 9] The manufacture approach of the ferroelectric thin film characterized by controlling the c-axis oriented component and orientation (117) component of a stacking tendency of a ferroelectric crystal in this ferroelectric thin film by said ferroelectric crystal's consisting of a titanic-acid bismuth, and changing the presentation ratio of Bi/Ti in said ferroelectric thin film in the or more 0.7 1.5 or less range in the manufacture approach of a ferroelectric thin film according to claim 8.
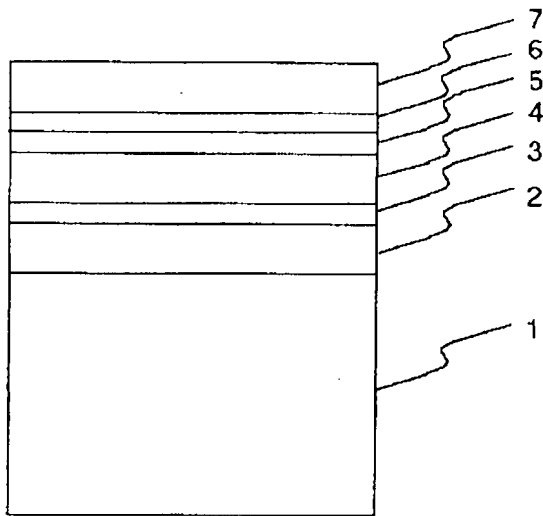[Claim 10] the manufacture approach of a ferroelectric thin film according to claim 9 -- setting -- MOCVD -- the manufacture approach of the ferroelectric thin film characterized by supplying Bi material gas and Ti material gas by law, forming said ferroelectric thin film on a substrate, and changing the presentation ratio of Bi/Ti in said ferroelectric thin film by [of Bi material gas at the time of this ferroelectric thin film formation, or Ti material gas] controlling one of the amount of supply at least.
[Claim 11] The manufacture approach of the ferroelectric thin film characterized by forming said ferroelectric thin film after forming the buffer layer which consists of titanium oxide on said substrate in the manufacture approach of a ferroelectric thin film according to claim 10.
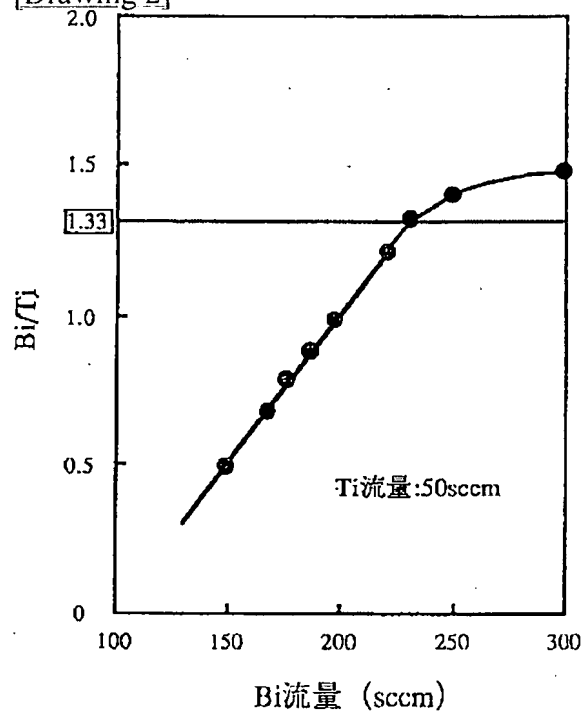[Claim 12] the crystalline-nucleus layer used as the growth nucleus of the ferroelectric crystal which forms the buffer layer which consists of titanium oxide on said substrate in the manufacture approach of a ferroelectric thin film according to claim 11, and accomplishes said ferroelectric thin film on this buffer layer -- 450-degree-C or more membrane formation temperature of 650 degrees C or less -- MOCVD -- the manufacture approach of the ferroelectric thin film characterized by forming said ferroelectric thin film on this crystalline-nucleus layer after forming by law.
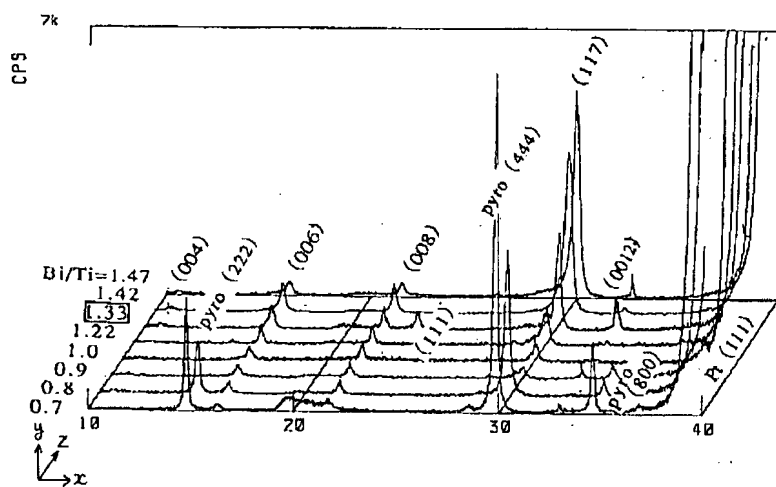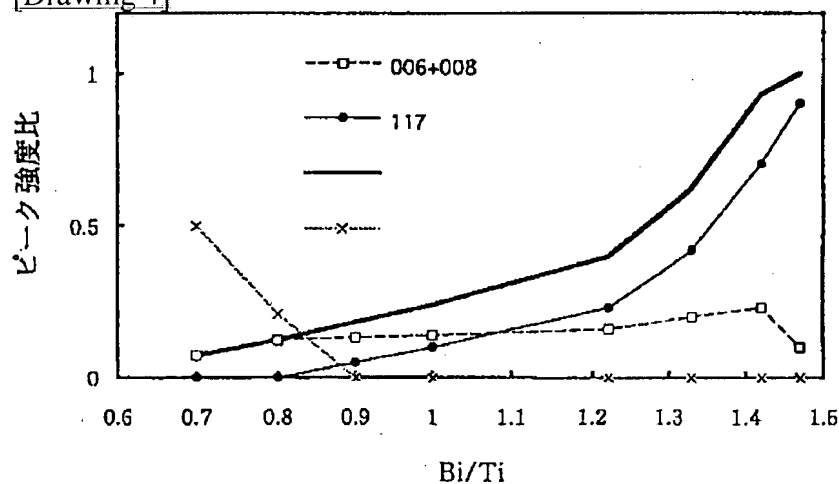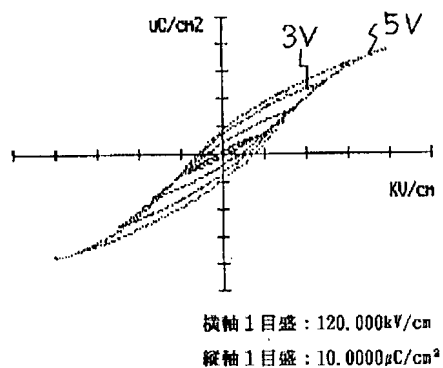
DRAWINGS

[Drawing 1]
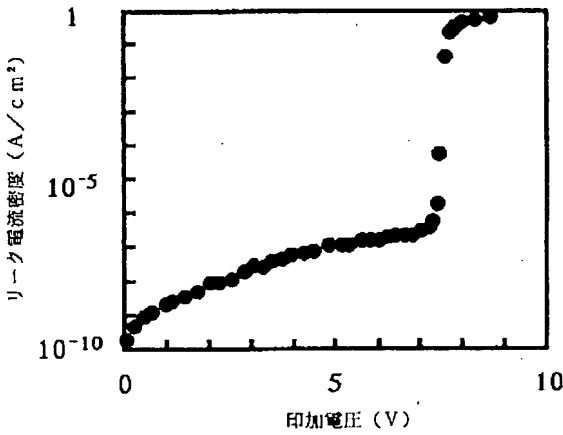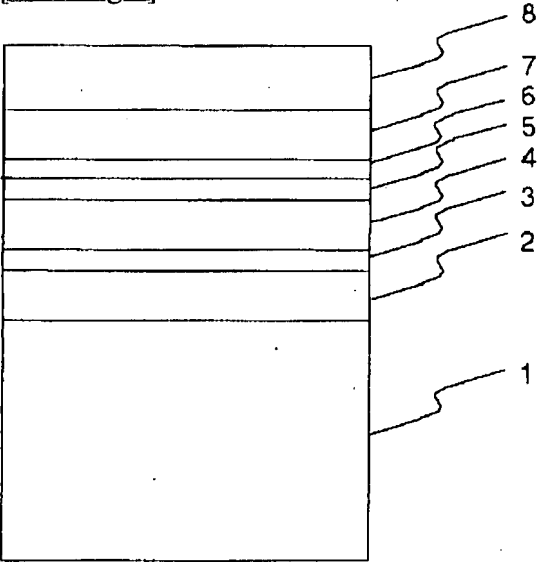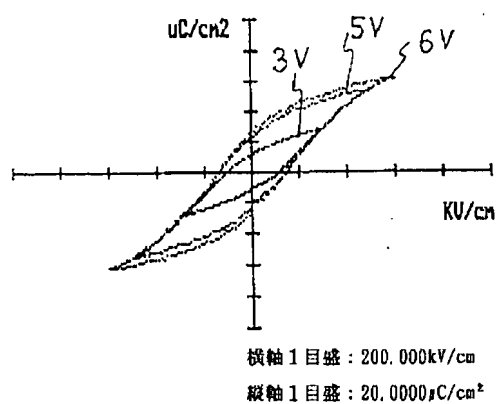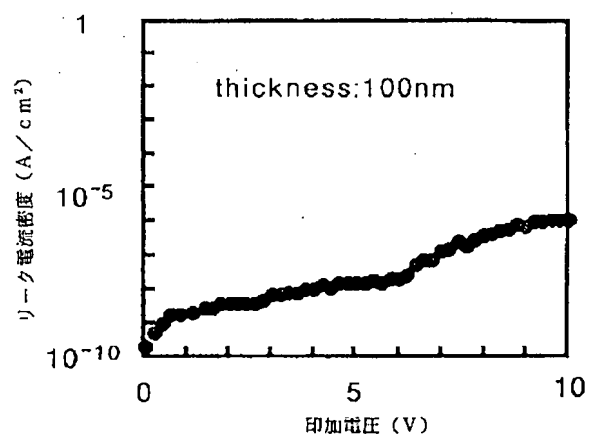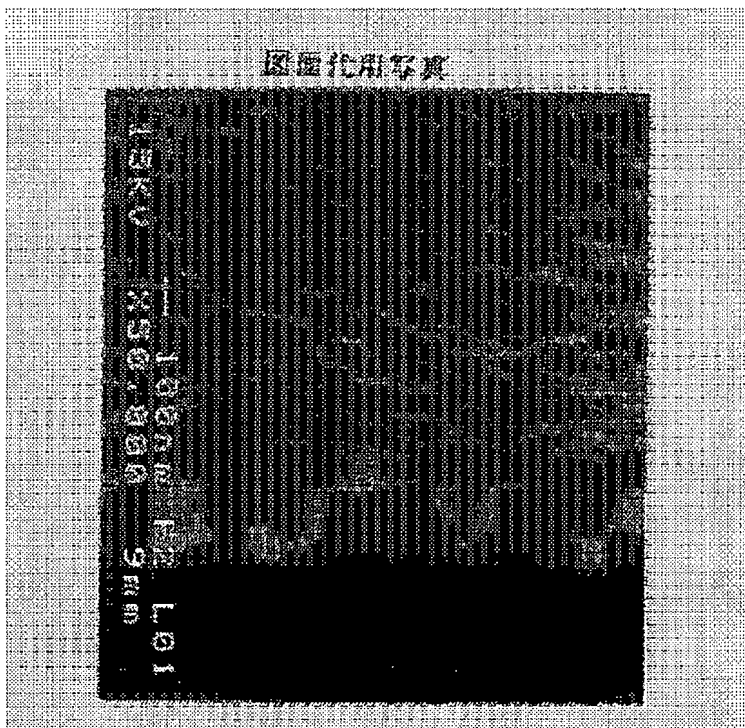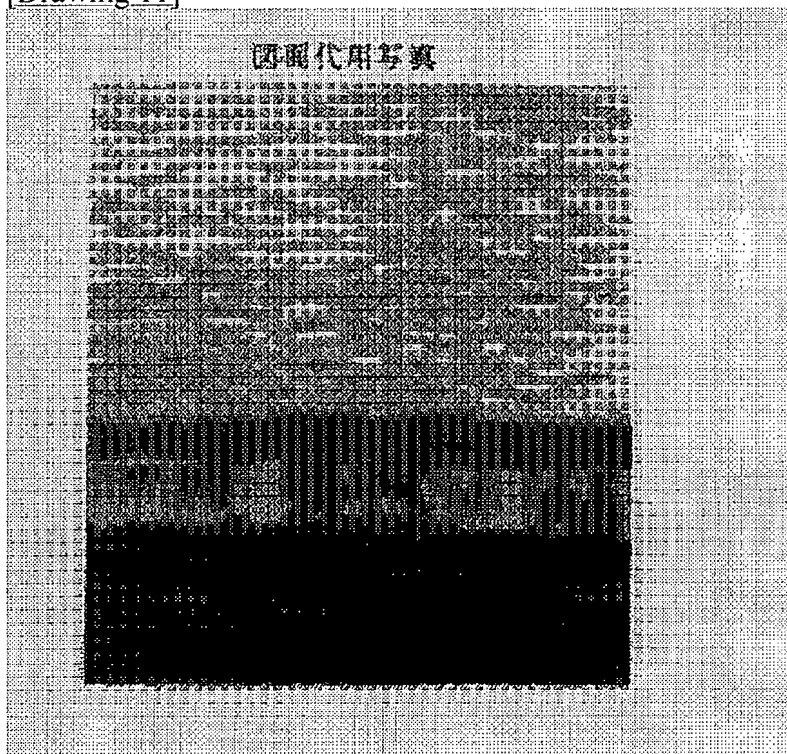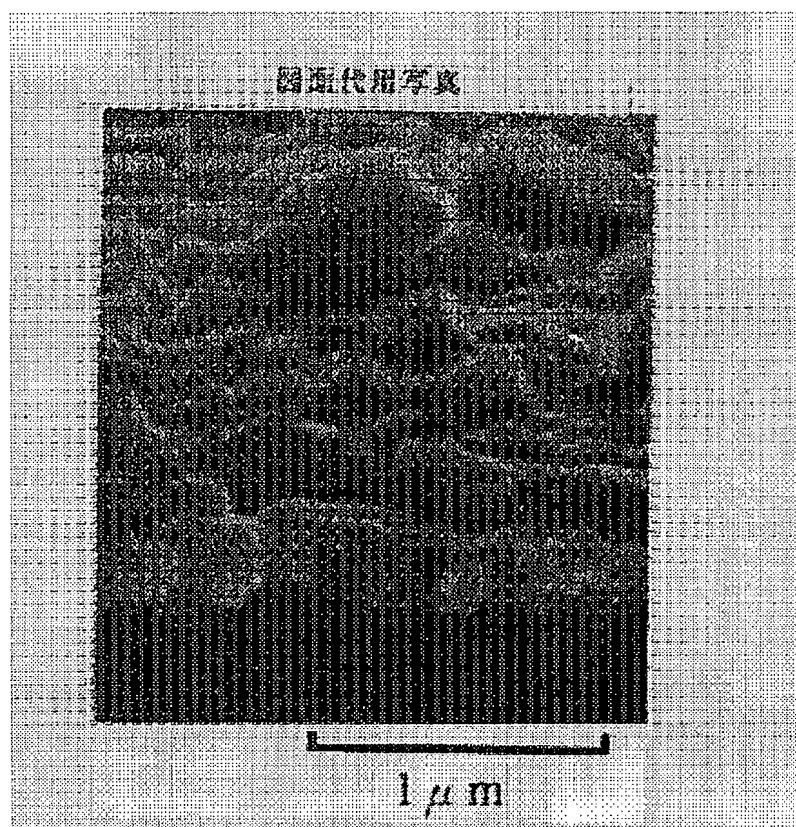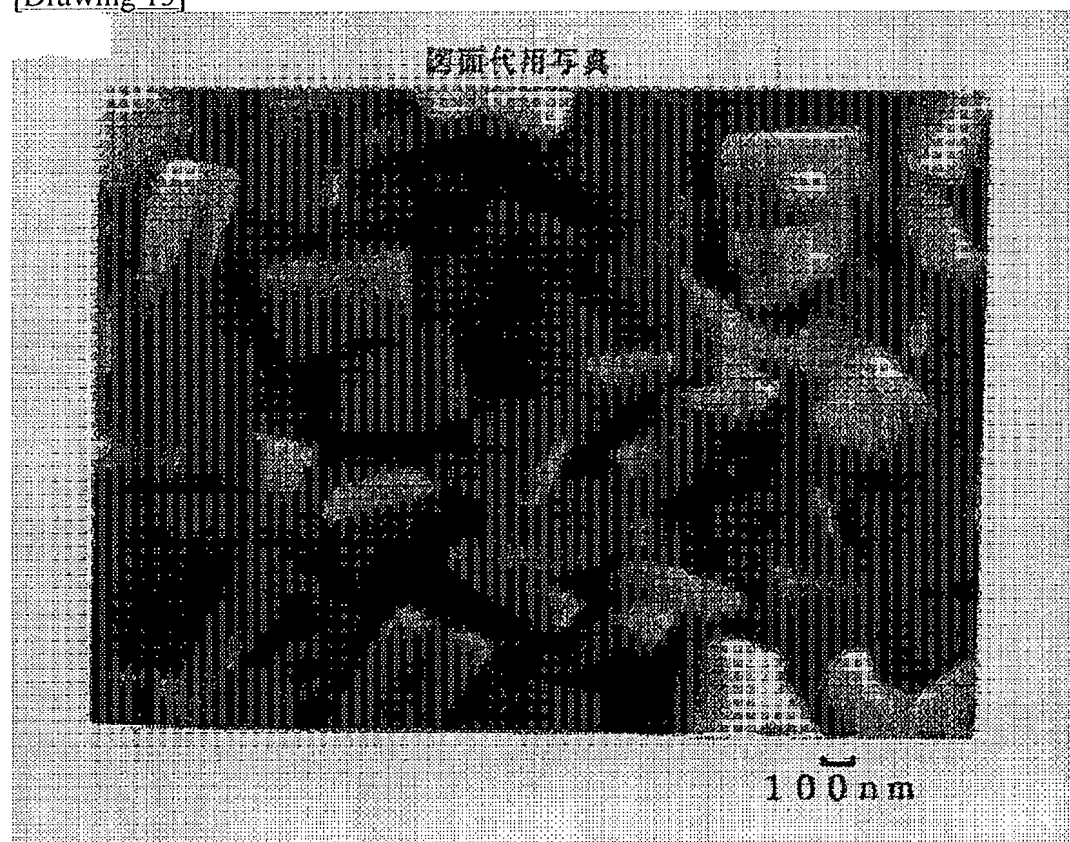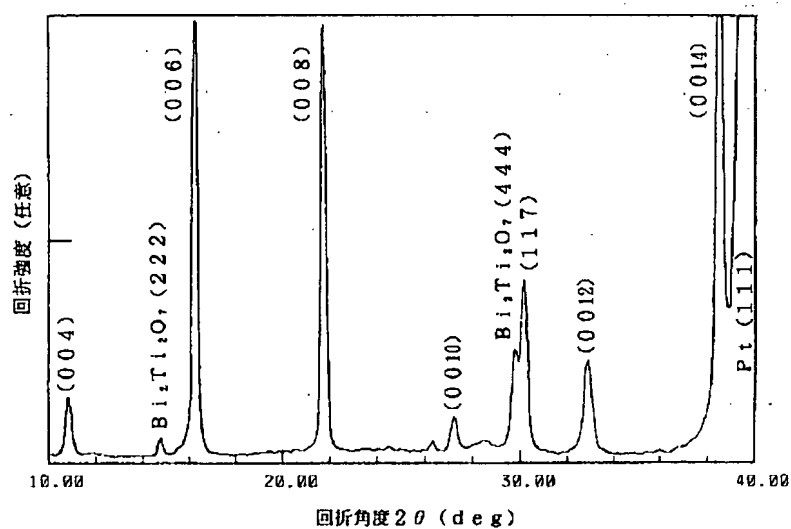

[Drawing 2]

[Drawing 3]

[Drawing 4]

[Drawing 6]

横軸1目盛：120.000kV/cm
縦軸1目盛：10.0000μC/cm²

[Drawing 7]

[Drawing 5]

[Drawing 8]

横軸1目盛：200.000kV/cm
縦軸1目盛：20.0000μC/cm²

[Drawing 9]

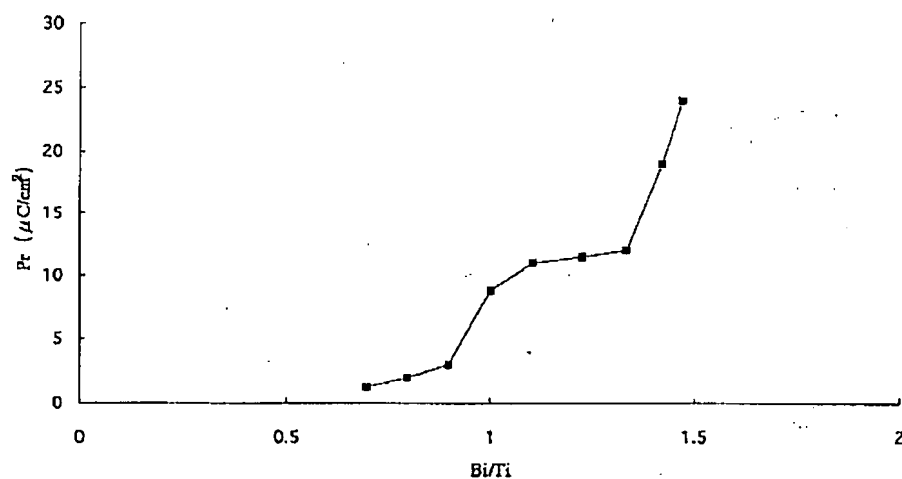[Drawing 10]

図面代用写真

[Drawing 11]

図面代用写真

[Drawing 12]

1μm

[Drawing 13]

100nm

[Drawing 14]

[Drawing 15]

[Drawing 16]